

PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Improvements in or relating to Electroplating Aluminium with Copper or Chromium

We, GAF CORPORATION, formerly General Aniline & Film Corporation, a corporation organized under the laws of the State of Delaware, United States of America of 140
5 West 51st Street, City, County and State of New York, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and
10 by the following statement:—

The present invention relates in general to protective coatings and more particularly to resin-based protective coatings advantageously adapted for use in connection with
15 coating operations requiring the deposition of metal upon metal.

A wide variety of methods for effecting metal to metal coating operations are well known in the art. Thus, it is common knowledge that the deposition of metal upon metal can be carried out by implementation of a number of techniques including, for example, electrodeposition or dip coating. The particular method selected will, of course, depend upon a number of considerations with perhaps the paramount criteria relating to the nature of the coating desired. Otherwise stated, the feasibility of a given coating method will depend, *inter alia*, upon the type
20 of metal serving as the base material, the type of coating to be deposited, the physical extent of the metallic film to be deposited, i.e., whether all or only pre-selected surfaces
25 of the base material are to be coated. In those instances wherein the entire surface area of the metallic article is to be coated, i.e., wherein complete immersion of the metallic article in the plating bath is indicated, it is quite likely that any of the con-

ventional coating techniques promulgated for such purposes is eminently applicable.

In contradistinction, the industrial applications are legion wherein metal on metal deposition is desirably effected upon only pre-selected surfaces of the metallic article. Moreover, the particular application may require that only discrete areas of a given metal surface be so coated as would be the case for example when providing ornamental or decorative designs. As will be readily apparent, the utilization of coating techniques which require immersing the entire metallic article in the plating medium, e.g. for electroplating, would not be feasible in the absence of some manipulative technique designed to locally immunize such metallic article against the effect of the plating medium. Heretofore, a wide variety of techniques has been evolved in the art by which such localized immersion can be accomplished. Paramount among the manipulative techniques thus far evolved in this regard are those based upon the use of protective coatings of a temporary nature, in the sense of being unaffected by prolonged contact with the solution media employed in the coating operation but which are nevertheless easily removed by suitable post-coating treatment. Invariably, such protective coating compositions contain as the essential ingredient a film-forming, polymeric resinous material, either natural or synthetic, capable of forming a strong, adhesive bond with the metal article being coated.

Despite the relatively widespread commercial acceptance of methods based upon the employment of temporary protective resin coatings, considerable difficulty has nevertheless been encountered. In the main, the resinous materials thus far employed for such purposes fail to provide the requisite measure

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of protection, i.e., metal surfaces coated therewith will usually exhibit some degree of metal deposition. As will be readily appreciated, it is of utmost importance that the protective resin coating be substantially, if not completely, impermeable to the plating bath in order to exclude even the remotest possibility of spurious metal deposition. Moreover, in many cases, it has been ascertained that the degree of adhesion extant between the resin coating and the metal surface tends to diminish to an intolerable extent, such a tendency being particularly manifest with the use of even moderately severe conditions of operation, e.g., temperature, period of immersion and solution corrosivity.

A further source of difficulty stems from the fact that many of the resin materials currently employed for the afore-described purposes exhibit undesirable change in solubility characteristics as a result of prolonged immersion in the plating bath to the extent that complete removal of the protective resin coating from the metal surface is rendered extremely difficult. As a consequence there is often a need to resort to mechanical, e.g., abrading as opposed to purely chemical, i.e., solubilization techniques to ensure such removal. Such techniques are in most instances burdensome both from the standpoint of economics as well as ease of processing.

The foregoing situation has proved to be of special consequence in connection with the production of bimetallic plates contemplated for ultimate use in the photomechanical reproduction arts, i.e., the preparation of photomechanical printing plates. Conventionally, such printing plates comprise for example an aluminium base provided on one side with a surface coating of copper or chromium, such surface coating serving as the support for a light-sensitive, resist-forming layer. An integral phase in the processing of such sensitized elements involves the etching out of the surface metal coating, this being accomplished pursuant to the provision of a final plate having grease-repellent and grease-receptive areas. However, as mentioned hereinbefore, the techniques heretofore provided for the preparation of such bi-metallic base plates have left much to be desired.

The present invention provides improved, resin-containing protective coatings admirably suited for use in connection with metal to metal coating operations and wherein one or more of the surfaces of such metal is to be protected against the plating medium.

The improved resin-containing protective coatings of the invention which are of a temporary nature are advantageously adapted for use in connection with the preparation of bimetallic plates where such resin is completely unaffected by the metal plating medium, e.g., the electrolytic plate bath; forms an adhesion bond of exceptional

strength with the metal being coated; and is capable of being easily and completely removed from the metal surface subsequent to the plating operation.

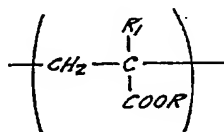
According to this invention we provide a process of electroplating an aluminium article with copper or chromium, the electroplating being carried out at an acid pH, which comprises employing as the cathode an oxide-free aluminium article having coated thereon in areas not required for electroplating a protective layer comprising a film-forming alkaline-soluble acrylic resin containing on a mole basis from 80% to 99% of acrylate or substituted acrylate units and from 1 to 20% of acrylic acid or substituted acrylic acid units, the said resin being capable of forming a strong, adhesive bond with the aluminium surface and being capable of being completely removed from the aluminium surface subsequent to the electroplating operation by subjecting same to an alkaline medium maintained at a pH of at least 7.5. The electroplating may be carried out at a temperature above ambient temperature.

In accordance with the present invention, it has been ascertained that the use of the said resins, and especially in coating operations involving the application of a metallic coating to one side of an aluminium base, leads to a considerable reduction in processing time as well as materials handling. For example, it has been found that the said resin materials are completely unaffected by the plating solutions conventionally employed in the copper coating of aluminium. As is well known, such plating solutions are usually one of four types viz. copper cyanide, copper sulphate, copper fluoborate or copper pyrophosphate. Not only do such resin materials serve as effective diffusion barrier layers, but in addition, retain a firmly adherent bonding with the aluminium surface throughout the entire plating operation. Perhaps the salient advantage attending the use of such resin materials relates to their ready solubility in alkaline media. Thus, immediately following completion of the plating operation, e.g., electrodeposition of copper on aluminium, the protective resin coating can be easily removed by treating same with an alkaline media, e.g., an ammonium hydroxide solution having a pH ranging from 7.5 to 9.0.

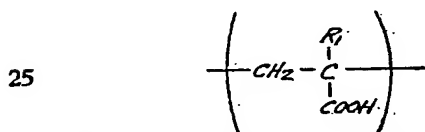
The film-forming alkaline soluble resin materials contemplated for use in accordance with the present invention are preferably derived from the polymerization of monomers such as acrylic acid, methacrylic acid, methylacrylate, ethylacrylate, butylacrylate, methylmethacrylate, ethylmethacrylate and butylmethacrylate to provide the required film-forming alkaline soluble acrylic resin containing on a mole basis from 80% to 99% of acrylate or substituted acrylate units and

from 1 to 20% of acrylic acid or substituted acrylic acid units.

- Resins of this type are readily available commercially such as the product "Carbo-
 5 set" from the B.F. Goodrich Chemical Corp. e.g., "Carbaset" 525. Although beneficial results may be obtained with the use of alkaline soluble resins of the general type encom-
 10 passed in the preceding paragraph, it has nevertheless been determined that optimum realization of the improvements made possible by the present invention are obtained with those polymeric materials containing within
 15 their skeletal structure, on a mole basis, from 80% to 99% of units of the following structural formula:



- wherein R represents hydrocarbon e.g., alkyl, aralkyl, aryl and alkaryl and preferably lower
 20 alkyl of 1 to 4 carbon atoms inclusive, e.g., methyl, ethyl, propyl, butyl, and wherein R₁ represents lower alkyl of 1 to 4 carbon atoms inclusive, and from 1% to 20% of units of the following structural formula:



wherein R₁ has the above defined significance.

- As will be recognized, the presence of the carboxyl groups may result from the fact that a corresponding proportion of acrylic acid type monomers was present in the initial
 30 polymerizable monomer mixture or alternatively, such carboxy groups may be introduced into the polymer skeletal chain by subjecting an acrylate polymer, i.e., one contain-
 35 ing no free acid group, to a suitable hydrolysis

80	Carbaset 525*	0.75 % in	isopropyl alcohol	98.0 parts
	"Alkaterge" A	1 % in	isopropyl alcohol	1.0 parts
	Oleic acid	2 % in	isopropyl alcohol	1.0 parts

- Approximately 5cc of the above composition is employed per sq. ft. of area to be
 85 coated. The coating is then allowed to dry for a period of about 15 to 20 minutes. The aluminium plate thus coated is immersed in a plating bath of the copper sulphate type, the aluminium serving as the cathode, the

95	Copper sulphate . 5H ₂ O	200 gms.
	Sulphuric acid	70 gms.
	Water to make	1 liter
	Cathode current density	30 amp./per sq. ft.
	Anode current density	30 amp./per sq. ft.
100	Bath temperature	85/90° F

after treatment. The manner in which the polymer is prepared is not a critical factor in the practice of the present invention so long as the relative proportions of carboxy solubilizing substituents in the polymer chain
 40 are maintained as above. Furthermore, the acrylate monomers may be employed in admixtures of 2, 3 or more. Thus, methyl acrylate; ethyl acrylate, butyl acrylate monomer systems have been found to provide
 45 polymers eminently suited to the purposes of the present invention. The resin is applied in the form of an 0.5 to 1% by weight solution in isopropyl alcohol, although other solvents such as: methanol, ethanol, acetone,
 50 diacetone alcohol, methyl "Cellosolve", dioxane, cyclohexanol and ethyl acetate may be used. The addition of a small quantity of oleic acid and a surface-active agent such as "Alkaterge" A (Commercial Solvents Corporation) is advantageous in promoting uni-
 55 form wetting when the resin is applied to the metal surface. The molecular weight of the resinous material is likewise not of critical importance so long as it be capable of depositing continuous films from solvent media.
 60 Thus, the molecular weight may range from 5,000 to 10,000 up to several million. As a general recommendation, however, resin materials having a molecular weight of from
 65 500,000 to 1,000,000 are preferred. "Cellosolve" and "Alkaterge" are Trade Marks.

The present invention will be further illustrated by the following examples.

EXAMPLE I

This Example illustrates the application of the present invention to the production of a copper-coated aluminium plate. An aluminium plate, the surfaces of which have been rendered oxide-free by dipping in sodium
 75 hydroxide solution, is flow-coated on one side with a protective coating comprising the following compositions:

anode being an oxide-free, high-purity copper, with the uncoated aluminium surface facing
 90 the anode.

The conditions and parameters of the electroplating operation are summarized as follows:

*Molecular weight approximately 800,000 as determined by light scattering.

The plating operation is carried out for a period of approximately 3 minutes. The aluminium cathode is removed from the plating bath and given a water rinse. Visual examination of the copper coated aluminium sheet revealed that the protective resin layer had remained intact throughout the entire electroplating treatment being totally unaffected by the plating solution.

Furthermore, the adhesion of the resin coating to the aluminium surface is in no way deleteriously affected. Despite the strong adhesive bond, the protective resin coating is easily and completely removed from the aluminium surface by swabbing with a pad which has previously been dipped in an ammonium hydroxide solution having a pH of

about 7.8. Resin removal is complete by the solvent-swabbing treatment to the extent that a polished aluminium surface is obtained merely by wiping with a cotton cloth. Thus, it is readily apparent that the alkaline solubility of the resin material remains unchanged despite subjection to the plating medium. The total time consumed in removing the protective resin coating is approximately 45 seconds.

EXAMPLE II

A resin pre-coated aluminium sheet is prepared in the manner described in Example I. Copper plating of the coated aluminium surface is carried out with the following plating solution utilizing the parameters indicated.

Copper fluoborate	224 gms.
Fluoboric acid	15 gms.
Boric acid	15 gms.
Water to make	1 litre
Cathode current density	35 amps. per sq. ft.
Anode current density	30 amps. per sq. ft.
Temperature	85°F.

The pH of the above solution is approximately 1.4. After electrodeposition of the copper film on the unprotected aluminium surface is complete, i.e., after a period of approximately 3 minutes, the aluminium cathode is removed from the bath and given a water rinse. Removal of the protective resin coating is accomplished in the manner described in Example I. Similar results are obtained in terms of ease of resin removal as well as resistance of the protective resin to the effects of the plating medium.

alkaline pH of at least 7.5, preferably up to 8.

Moreover, the nature of the plating bath is likewise not a critical factor in the practice of the present invention, the sole requirement being that such bath be maintained under an acid pH and preferably below 6.5.

The present invention may be applied to production of metal surfaces containing ornamental or decorative designs thereon. The metal to be coated need not be planar but may be of arcuate or otherwise irregular configuration. In such instances, the resin may be suitably applied by the use of a suitable stencil or pattern. The procedure employed would be similar to that described in the above Examples both as regards the electroplating operation and the protective resin removal operation.

EXAMPLES III and IV

Examples I and II are repeated utilizing a protective coating composition containing as the resin component a polymer containing, on a mole basis, 90.4% of a mixture of methyl acrylate, ethyl acrylate and butyl acrylate polymer units and 9.6% acrylic acid polymer units. Following the electroplating operation, resin removal is readily accomplished by swabbing with a cotton cloth which has been previously saturated with an ammonium hydroxide solution having a pH of 7.5.

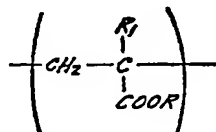
Results similar to those described in the above Examples are obtained when utilizing a chromium plating bath maintained under an acid pH. It will be understood that the nature of the alkali employed in the resin-removal step is not particularly critical and accordingly, may be selected from a wide variety of materials, e.g., alkali metal hydroxides such as sodium hydroxide, potassium hydroxide or trisodium phosphate. The important consideration in this regard is that the resin-removal bath be maintained at an

WHAT WE CLAIM IS:—

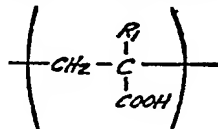
1. A process of electroplating an aluminium article with copper or chromium, the electroplating being carried out at an acid pH, which comprises employing as the cathode an oxide-free aluminium article having coated thereon in areas not required for electroplating a protective layer comprising a film-forming alkaline-soluble acrylic resin containing on a mole basis from 80% to 99% of acrylate or substituted acrylate units and from 1 to 20% of acrylic acid or substituted acrylic acid units, the said resin being capable of forming a strong, adhesive bond with the aluminium surface and being capable of being completely removed from the aluminium surface subsequent to the electroplating opera-

tion by subjecting same to an alkaline medium maintained at a pH of at least 7.5.

2. The process according to Claim 1, wherein the acrylate units correspond to the structural formula:



- wherein R represents hydrocarbon and R₁ represents alkyl containing up to 4 carbon atoms inclusive, and the said acrylic acid units correspond to the structural formula:



wherein R₁ has the same significance as before.

3. The process according to Claim 2, wherein the acrylate units comprise a mixture of methyl acrylate, ethyl acrylate and butyl acrylate.

4. The process according to Claim 1, wherein the electroplating is carried out at a temperature above ambient temperature.

5. The process of electroplating as claimed in Claim 1 substantially as herein described and exemplified.

6. An electroplated aluminium article obtained by the process claimed in any preceding claim.

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